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Fate of Carbaryl, 1-Naphthol, and Atrazine in Seawater[1]

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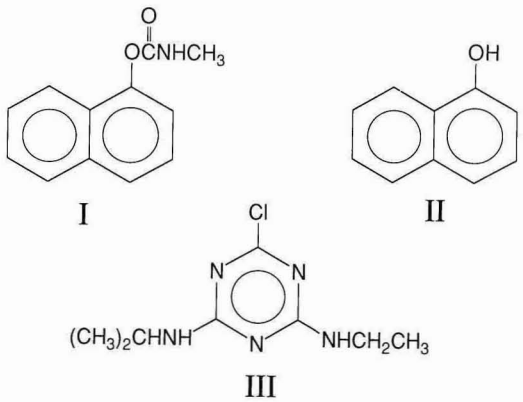
ABSTRACT: The fate of carbaryl, 1-naphthol, and atrazine was determined under light and dark conditions in filter-sterilized and raw (unfiltered) seawater. Carbaryl was hydrolyzed in the dark, quantitatively, to 1-naphthol with a half-life of 24 hr at pH 7.9 or 23 hr at pH 8.2 (24°C). Naphthol was stable in the dark in sterile seawater, but was degraded to undetectable levels in 96 hr in raw seawater. In artificial sunlight, carbaryl degraded with a half-life of 5 hr and 1-naphthol was completely degraded after 2 hr. No further degradation products were observed for either compound. Atrazine was stable under light and dark conditions in sterile seawater; however, in raw seawater, it was degraded by 23% after 96 hr. These data suggest that atrazine may be stable enough in seawater to permit exposure of susceptible marine life, while, in the presence of sunlight, carbaryl and 1-naphthol would rapidly dissipate to undetectable levels.

EACH YEAR, PESTICIDES ARE USED heavily on crops in the Hawaiian Islands, and many also are used in backyard gardening by the general public. It is reasonable to assume that these chemicals make their way into the ocean by way of agricultural drainage and urban runoff. The effects of trace levels of pesticides on coral have not been addressed, but, before considering this question, it is important to know what happens to the chemicals to which corals may be exposed. The basic question concerns the stability of the pesticide in seawater, for, if it rapidly breaks down, it will not be bioavailable. Breakdown rates and products are important, as degradation products sometimes are more toxic than the parent compound.

The goal of this project was to determine the stability of two common pesticides in seawater. Carbaryl (I), the active ingredient in the pesticide Sevin®, is used commercially and is also widely available for home and garden use as shown by a casual survey of local stores. Two papers have previously reported the degradation of carbaryl in seawater (Glod and Pawlak 1983, Samanidou and Fytianos 1988), but not under environmentally relevant conditions. Atrazine (III) also is widely applied to crops in the Hawaiian Islands (C. J. Miles, pers. comm.). In addition, we investigated the stability of 1-naphthol (II), a degradation product of carbaryl (Wolfe et al. 1978) that has been shown in some cases to be more toxic to marine organisms than was the parent compound (Stewart et al. 1967).



SCHEME 1.

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MATERIALS AND METHODS

Materials

Pure analytical standards of carbaryl and atrazine were donated by Dr. Carl Miles of the University of Hawaii at Manoa. 1-Naphthol (99+%) was purchased from Aldrich Chemical Co., found to be pure by high-performance liquid chromatography (HPLC), and used as received. Solid phase extraction cartridges (J. T. Baker), 3 ml C-8 (500 mg), were purchased from VWR Scientific. All solvents were HPLC grade and used as received from Fisher Scientific Co. Filtered (0.22 μm) seawater for biodegradation and hydrolysis measurements was obtained at the Hawaii Institute of Marine Biology, Kaneohe, Hawaii; that for photolysis experiments was from the Bodega Bay Marine Laboratory, Bodega Bay, California.

Extraction

Aliquots (25 ml) of either raw seawater or 0.22-μm–filtered seawater containing each chemical at 5×10^{-7} M were drawn under vacuum through a solid phase extraction cartridge preconditioned by flushing with two

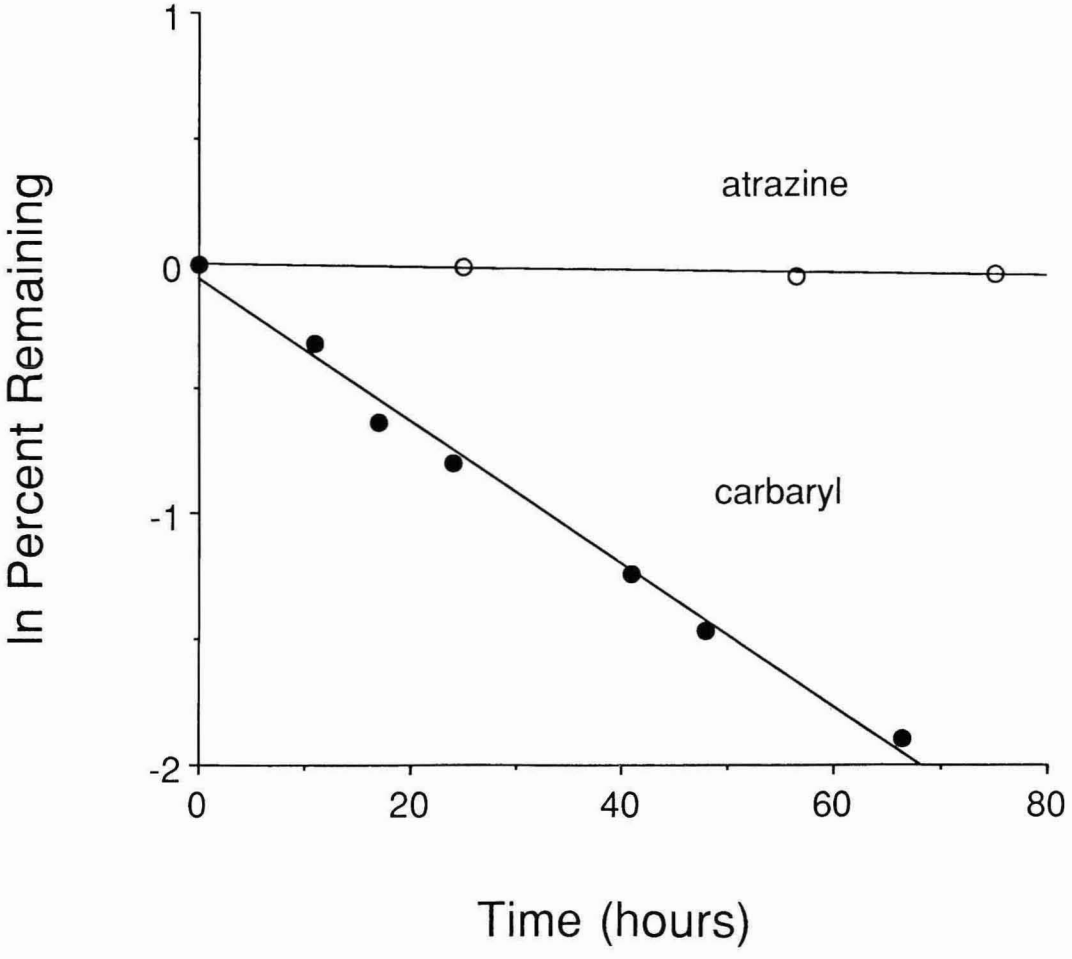

FIGURE 1. Rate of hydrolysis of carbaryl ($t_{1/2}$ = 24 hr) and atrazine based upon pseudo-first-order kinetics.

column volumes each of acetonitrile, methanol, and finally distilled water. The sample flask was rinsed with distilled water and the rinsate also was drawn through the cartridge. Residual water was removed by centrifugation at high speed for 1 min, the pesticide eluted from the cartridge with 0.5 ml of acetonitrile, the eluate transferred to a 2-ml borosilicate glass vial fitted with a Teflon-lined silicone-rubber cap, and the contents analyzed by HPLC.

Analysis

HPLC analysis was conducted with a Beckman Model 110B instrument. Injections (10 μl) were made onto a 250 mm × 4.6 mm, 5-μm Econosphere C-18 column (Alltech Associates, Inc.). The solvent composition for carbaryl and 1-naphthol was acetonitrile-1% aqueous glacial acetic acid (1:1), with detection by UV absorbance at 285 nm. For atrazine, the solvent composition was acetonitrile-water (3:2) with detection at 254 nm. In all cases, the flow rate was 1 ml/min.

Hydrolysis

Solutions of each pesticide at 5×10^{-7} M in 1 liter of 0.22-μm–filtered seawater were placed into bottles wrapped with aluminum foil to exclude sunlight and placed on water tables to maintain the temperature of ambient seawater (24°C). Samples were withdrawn at timed intervals, extracted, and analyzed as above. Biodegradation was measured identically to hydrolysis except that raw (unfiltered) seawater replaced filtered seawater.

Photolysis

Solutions at 5×10^{-7} M of each pesticide in 0.22-μm–filtered seawater were placed in a

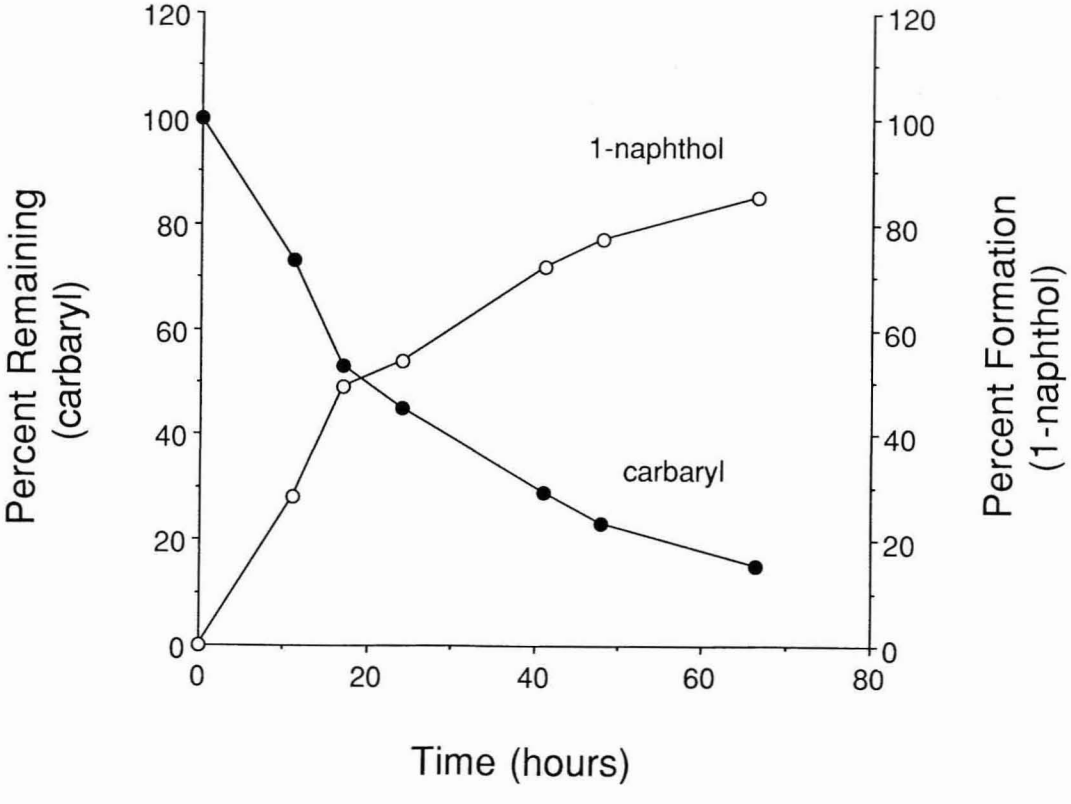

FIGURE 2. Quantitative formation of 1-naphthol from the hydrolysis of carbaryl.

1.5-liter, constant-temperature (24°C) photoreactor described by Crosby and Tang (1969) equipped with a F40BL fluorescent UV lamp that mimicked the spectral transmission of sunlight between 290 nm and 360 nm (Light Sources, Inc. 1989). Dark controls were run simultaneously. At timed intervals, samples were withdrawn, extracted, and analyzed as above.

RESULTS AND DISCUSSION

Hydrolysis

Recoveries from seawater were consistently >95% for atrazine, carbaryl, and 1-naphthol. Over a 3-day period, atrazine showed a negligible loss while carbaryl appeared to be hydrolyzed according to pseudo-first-order kinetics with a half-life of 24 hr at pH = 7.9 (Figure 1) or 23 hr at pH = 8.2 (data not shown). Pseudo-first-order kinetics are due to the strong buffering action of seawater, as the pH was not observed to change over the course of an experiment. In each case, 1-naphthol was formed in quantitative yield (Figure 2) and was not degraded over the course of 3 days. These data agree with those reported previously by Stewart et al. (1967), who found 1-naphthol to be stable in seawater (light excluded) for 24 hr.

Biodegradation

In raw seawater, both carbaryl and 1-naphthol were degraded to undetectable levels within 96 hr and atrazine was degraded by ca.

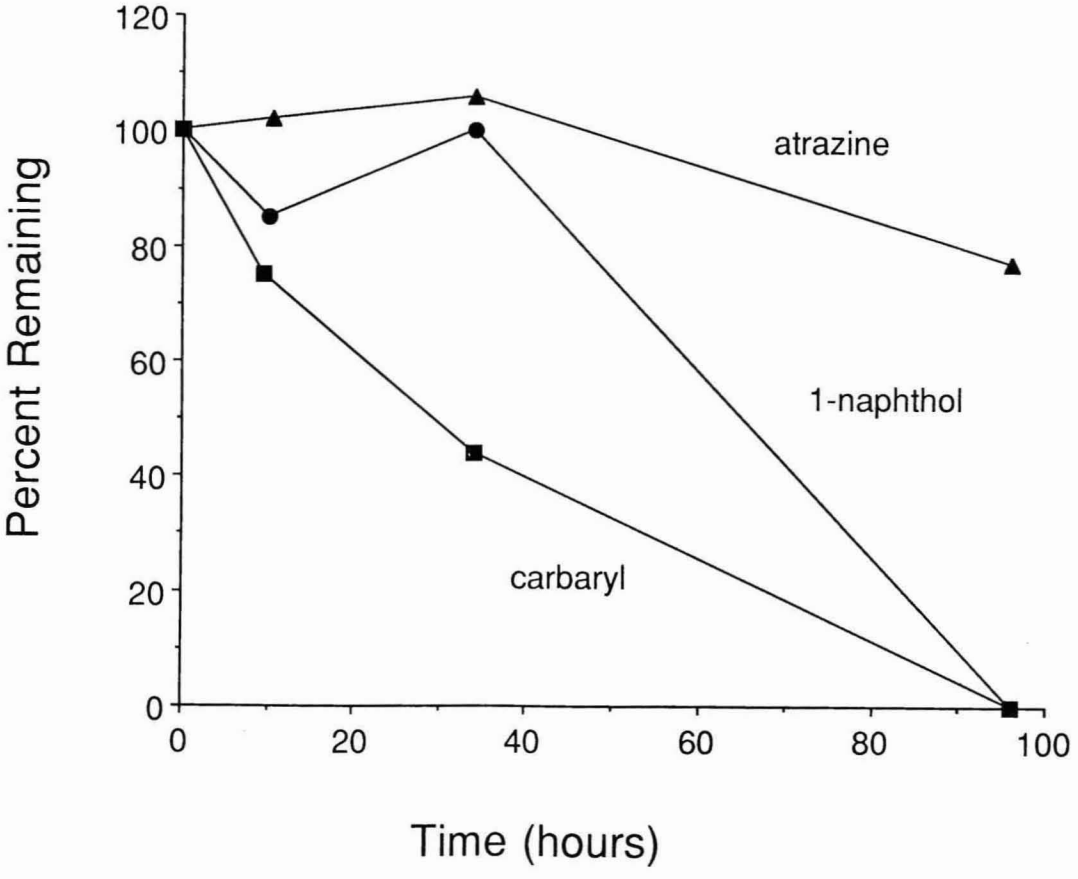

FIGURE 3. Dissipation of carbaryl, atrazine, and 1-naphthol in raw seawater.

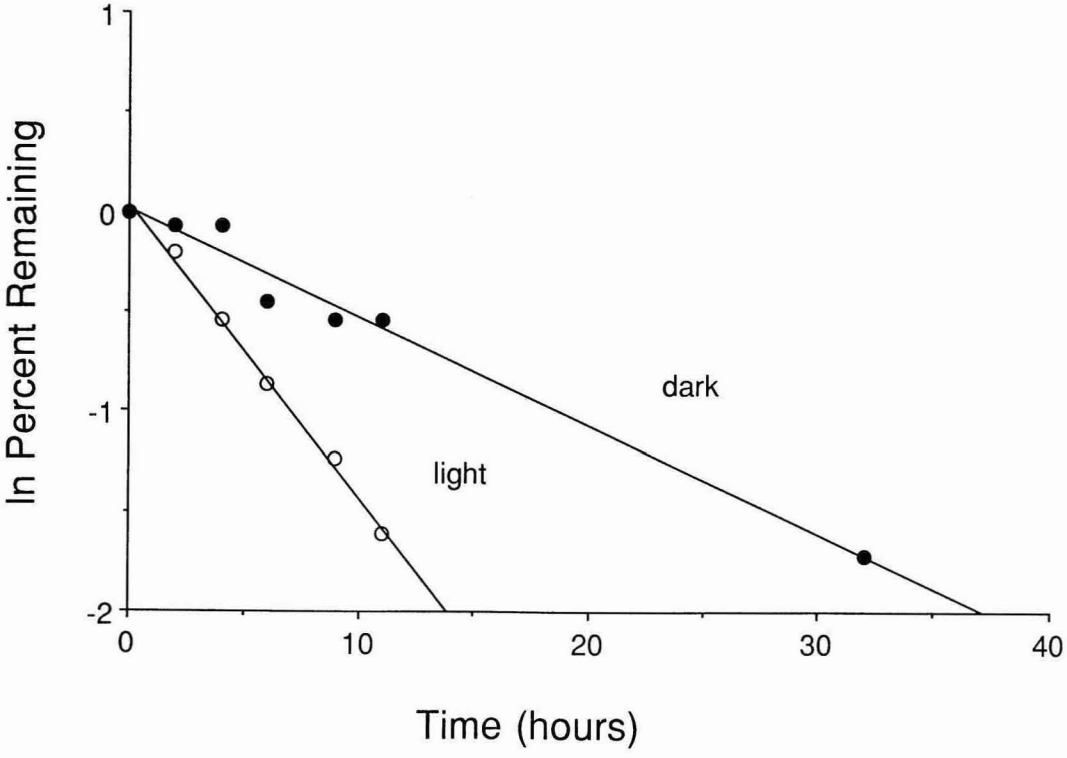

FIGURE 4. Rate of dissipation of carbaryl in the presence of UV radiation ($t_{1/2}$ = 5 hr).

23% (Figure 3). As both atrazine and 1-naphthol were stable to hydrolysis, it is assumed their disappearance from water is due to microbial metabolism. However, it is difficult to attribute this to biotic action only, as time points were not taken between 36 and 96 hr, and hydrolysis in filtered seawater was measured for 70 hr at the longest.

Photolysis

In the presence of ultraviolet radiation, 1-naphthol was degraded very quickly. Of the initial amount, 67% was degraded within 1 hr and, after 2 hr, 1-naphthol levels had fallen below the limit of detection; no breakdown products were observable by HPLC. In terms of environmental significance, it is unlikely that 1-naphthol would be persistent enough to have an impact on organisms in the presence of sunlight.

Carbaryl was degraded with a half-life of 5 hr (Figure 4). It is possible that this is due to direct photolysis, as the UV spectrum of carbaryl in seawater indicates that it slightly overlaps the sunlight region (Figure 5). The large overlap of the sunlight spectrum with that of 1-naphthol explains the rapid loss from water in the presence of light. There was no loss of atrazine in solutions exposed to UV irradiation or in dark controls. This observation also is explained by the UV absorption spectrum of atrazine in seawater (Figure 5), which does not overlap the spectrum of sunlight.

CONCLUSIONS

The fate of carbaryl in seawater appears to be governed by hydrolysis and photolysis, and, in a normal environmental situation, these processes would combine to degrade the compound completely over the course of a

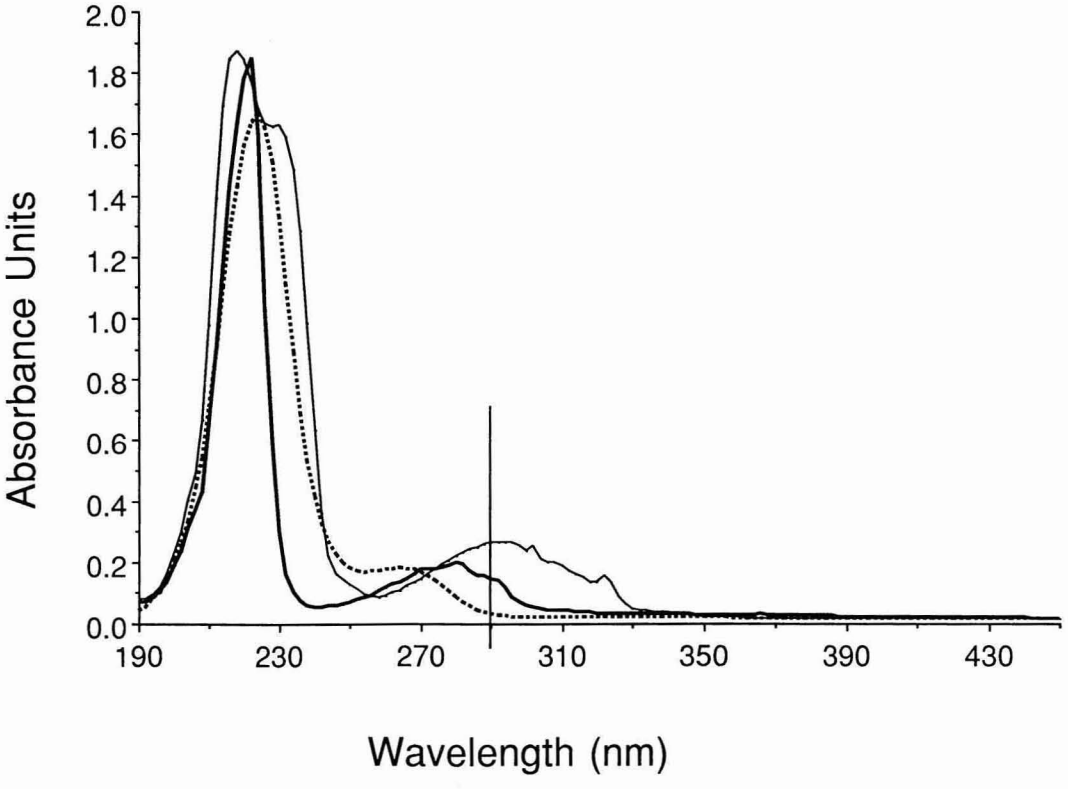

FIGURE 5. UV absorption spectra of carbaryl (heavy line, 1.7×10^{-5} M), 1-naphthol (light line, 1.4×10^{-5} M), and atrazine (dashed line, 2.6×10^{-5} M) in seawater. The vertical line at 290 nm indicates the lowest wavelength of sunlight reaching the surface of the ocean (Baker and Smith 1982).

day. The principal breakdown product, 1-naphthol, is degraded by sunlight almost immediately after formation, but appears to be stable for a period of days in the absence of light. This could be important in areas such as the Hawaiian Islands during periods of heavy and extended rainfall, where pesticide residue could be washed from an island and the cloud cover would retard photolysis. In this scenario, carbaryl and 1-naphthol might persist long enough to allow exposure of corals and other marine organisms. Considering the high toxicity of carbaryl to aquatic invertebrates (Mayer and Ellersieck 1986), research on the toxicity of these compounds to corals seems to be important; no data presently exist.

Atrazine, on the other hand, is persistent in water and resists both hydrolysis and photolysis. It breaks down slowly in raw seawater, presumably because of the action of microorganisms. Given this and the fact that it is one of the most heavily used pesticides in Hawaii, it could present a problem for aquatic plants and for those animals, such as coral, that rely on symbiotic algae; atrazine is a powerful photosynthesis inhibitor, but is not particularly toxic to aquatic animals (Mayer and Ellersieck 1986).

ACKNOWLEDGMENTS

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